

Soft X-Ray Fluorescence Measurements of Irradiated Polymer Films

R.P. Winarski¹, S. Stadler¹, D.L. Ederer¹, E.Z. Kurmaev²,
T.A. Callcott³, M.M. Grush³, A. Moewes⁴, and R.C.C. Perera⁵

¹Department of Physics, Tulane University, New Orleans, Louisiana 70118, USA

²Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620219 Yekaterinburg GSP-170, Russia

³Department of Physics, University of Tennessee, Knoxville, Tennessee 37996, USA

⁴Center for Advanced Microstructures and Devices/Louisiana State University,
Baton Rouge, Louisiana 70803, USA

⁵Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory,
Berkeley, California 94720, USA

INTRODUCTION

Polyimide films that are heavily irradiated by ions exhibit a significant increase in electrical conductivity nearing that of inorganic semiconductors [1-4]. It has been shown that ion irradiation induces marked changes in the chemical structure of the polyimide films and increased conductivity due to polymer carbonization [5-7]. Conversion of polycarbosilane films to ceramics by ion implantation leads to increased hardness and oxidation resistance [8]. It is thought that some of the carbon in the PCS film segregates during the irradiation and annealing processes, leading to different local structures and hybridization states.

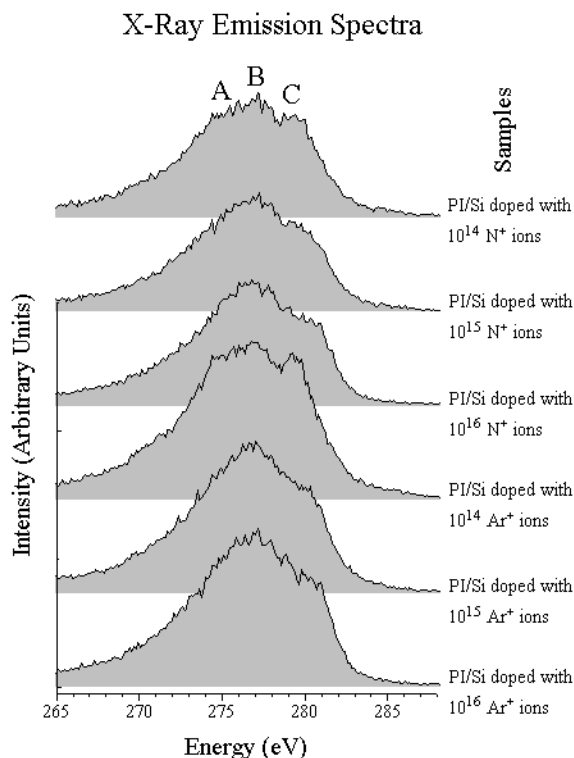
EXPERIMENTAL RESULTS

Fluorescent soft x-ray carbon K α emission(XES) and carbon 1s total fluorescent yield(TFY) spectra have been used to characterize the bonding of carbon atoms in polyimide(PI) and polycarbosilane(PCS) films. The PI films have been irradiated by nitrogen and argon ions with concentrations ranging from 1×10^{14} to 1×10^{16} ions/cm². The PCS films have been annealed to 1000° C and/or irradiated with 200 keV carbon ions to a concentration of 5×10^{15} ions/cm². We find that the fine structure of the carbon XES of the PI films changes with implanted ion concentrations above 1×10^{14} ions/cm² which we believe is due to bond degradation and the creation of carbon clusters in the films. The electrons in the atoms of these clusters fill unoccupied states in the valence and conduction bands and lead to a narrowing of the band gap. We find that the bonding of carbon atoms in the PCS films after carbon ion irradiation is similar to the bonding in diamond films, and the bonding after irradiation and subsequent annealing appears more like the bonding found in graphite-like silicon films. The non-irradiated PCS film that was annealed at 1000° C converts to a ceramic with the composition of amorphous Si_{0.77}C_{0.23}:H.

IRRADIATED POLYIMIDE FILMS

Soft x-ray emission spectroscopy is governed by the dipole selection rules, and because the excitation is site specific, the x-ray fluorescence can be used to gain information about the local bonding environment of a sample. XES probes the valence band states and can be compared with partial density of states calculations. The x-ray transitions are limited to the first coordination sphere of the emitting atom, and XES is therefore sensitive to short-range order. In this way, the technique can be used to examine changes in the local environment and chemical bonding of the emitting atom due to various thermal and physical treatments.

The results of measurements of the carbon K α XES of irradiated PI films are presented in Figure 1. The peak structure labeled by A, B, and C is only observed for implanted ion concentrations below 1×10^{14} ions/cm². The structure can be attributed to the occupied molecular orbitals(MO) of the polyimide chains, particularly the occupied states of the carbon 2p atomic orbitals which are probed by the 2p \rightarrow 1s transitions of the carbon K α XES.



The relative intensities of peaks A and C progressively decrease (with respect to peak B) for ion concentrations above 1×10^{14} ions/cm². Interestingly the changes in these features are the same for both ion types, indicating that the structural changes to the carbon atoms in these samples is not related to the ion-carbon bonding. We also noted a narrowing of the gap as determined from XES and TFY measurements as implanted ion concentrations increased. The XES for the 1×10^{16} ions/cm² samples resembled those of amorphous carbon films, suggesting the formation of carbon clusters in these prepared PI films [8].

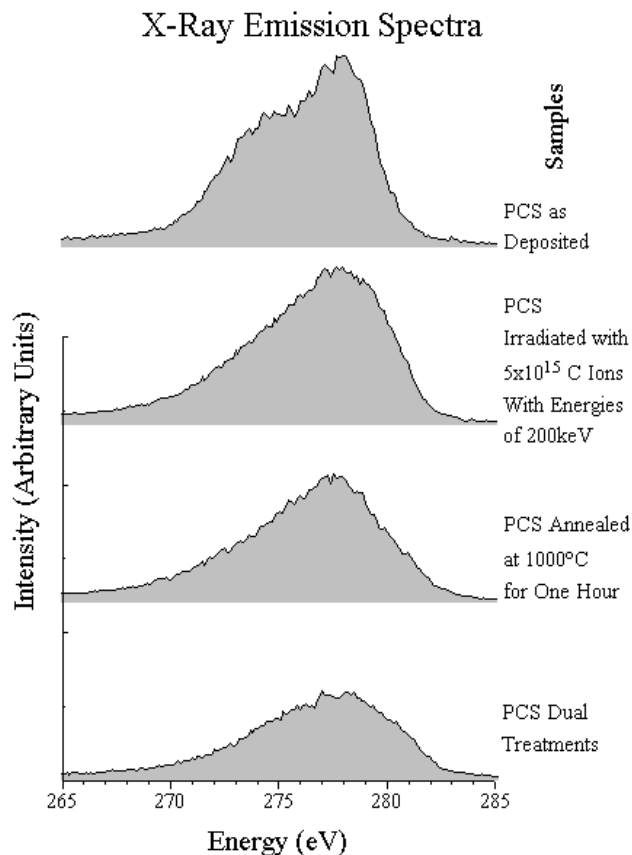
Figure 1. C K α XES for irradiated polyimide films. Note the change in shape of the spectra as the ion concentration increases.

IRRADIATED POLYCARBOSILANE FILMS

Measurements of the carbon K α XES of the PCS films are presented in Figure 2. The spectra exhibit distinct changes between deposited polymer films, annealed films (One hour at 1000° C), irradiated films (5×10^{15} ions/cm² concentration of 200 keV carbon ions), and combined treatment films (irradiation followed by annealing). According to infrared Raman measurements of these films, irradiation causes a segregation of some of the carbon atoms in the polymer resulting in a chemical state similar to that of a diamond-like film [9]. After a combined treatment, XES spectra of these films more closely resemble the features of a graphite-like spectrum. To investigate these conclusions we compared the carbon K α XES of the various PCS films with spectra from known samples of HOPG, silicidated graphite and diamond-like films [8].

Our carbon K α XES measurements confirm the results of the Raman spectra, in that the chemical states of the carbon atoms in irradiated PCS films resemble those of diamond-like films, and in combined treatment films they resemble graphite-like silicon systems. The spectra from our annealed PCS films show a conversion to an amorphous ceramic with the composition of Si_{0.77}C_{0.23}H [8].

Figure 2. C K α XES for PCS films. Note the change in shape of the spectra for different treatments (annealing and irradiation).



REFERENCES

1. J. Davenas and X.L. Xu, Nucl. Inst. Methods B 71 (1992) 33
2. V. Svorcik, V. Rubka, V. Hnatowicz, and J. Kvitek, Mat. Lett. 19 (1994) 329
3. T. Trigaud, J.P. Moliton, C. Jussiaux, and B. Maziere, Nucl. Inst. Methods B 107 (1996) 323
4. I.H. Loh, R.W. Oliver, and P. Sioshansi, Nucl. Inst. Methods B 34 (1988) 337
5. V. Svorcik, R. Endrst, V. Rybka, E. Arenholz, V. Hnatowicz, and F. Cerny, Eur. Polym. J. 31 (1995) 189
6. D. Xu, X.L. Xu, G.D. Du, R. Wang, S.C. Zou, and X.H. Liu, Nucl. Inst. Methods B 80/81 (1993) 1063
7. M. Iwaki, K. Yabe, A. Fukuda, H. Watanabe, A. Itoh, and M. Takeda, Nucl. Inst. Methods B 80/81 (1993) 1080
8. R.P. Winarski, D.L. Ederer, E.Z. Kurmaev, S.N. Shamin, T.A. Callcott, A. Moewes, J.-C. Pivin, and R.C.C. Perera (to be published).
9. J.-C. Pivin and P. Colombo, J. Am. Ceram. Soc. (In Press)

This work was supported by the Russian State Program "Atomic and Spatial Structures," Russian Science Foundation for Fundamental Research (Project 96-15-96598), a NATO Linkage Grant (HTECH.LG 971222), INTAS-RFBR (95-0565), NSF Grants (DMR-9017997 and DMR-9420425) and the DOE-EPSCOR and Louisiana Education Quality Special Fund (DOE-LEQSF (1993-95-03)). The experiments were conducted at Lawrence Berkeley National Laboratory's Advanced Light Source which is supported by the United States Department of Energy under contract (DE-AC03-76SF00098).

Principal investigator: Robert P. Winarski, Department of Physics, Tulane University. Email: rwinarsk@mailhost.tcs.tulane.edu. Telephone: 504-865-5520.